Micro-scale Li_2S -C composite preparation from Li_2SO_4 for cathode of lithium ion battery

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Abstract:

A facile and scalable method is proposed to prepare microscale Li_2S -C composite from Li_2SO_4 through carbon-thermal reduction, followed by a carbon coating process. Multi-solvent recrystallization was utilized to reduce the particle size of Li_2SO_4 to 2 μm . This fine-grain Li_2SO_4 helps to shorten the particle size of reduction product from 10 μm to 3 μm . Using fine Li_2SO_4 also brings the benefit of greatly reducing the over potential during the initial charge process and increasing the kinetics for Li_2S materials.

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3 Finally, the microscale $\text{Li}_2\text{S-C}$ composite prepared from fine Li_2SO_4 enables a stable
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6 capacity of 350 mAh g^{-1} at 0.2 C , higher than that obtained using a cathode prepared
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9 from commercial Li_2SO_4 .
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16 **Keywords:** $\text{Li}_2\text{S-C}$, lithium sulfide, Li_2SO_4 , carbon-thermal reduction
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25 **1. Introduction**

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35 With the emerging markets of electric vehicles and stationary energy-storage
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37 systems, improvements in energy density and safety of rechargeable batteries are
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39 urgently required. Li-S batteries are very promising electrochemical systems to provide
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41 specific energy, two-fold higher than that of commercial lithium ion batteries. [\[1-3\]](#)
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47 Li-S batteries can be manufactured in two ways: using a sulfur cathode coupled to a
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49 lithium metal or lithiated anode; or using a Li_2S cathode paired with a conventional
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51 carbon anode or new Si anode. The practical application of Li-S batteries has been
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54 hindered to date by several issues: dissolution of polysulfides into the electrolyte, low
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3 electronic and ionic conductivity, and significant volume changes. [4, 5] Materials
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6 design at the nano- and microscale is very effective to improve the performance of
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9 either sulfur or Li_2S cathode. Recently, encapsulating nano-/microstructured Li_2S or
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12 sulfur into carbonaceous shell/matrix has emerged as the most popular technique. [6-13]
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16 Li_2S cathodes have attracted large interest recently because they advantageously
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18 enable the use of lithium-free anodes. But the synthesis of Li_2S is much more difficult
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21 than that of sulfur because of its high reactivity and moisture sensitivity. It is rather
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24 difficult to prepare nanosized Li_2S from other chemicals. Up to now, there are no
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27 commonly applied methods or procedures to synthesize Li_2S . As a result, current
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30 researches mainly start from bulk Li_2S to prepare $\text{Li}_2\text{S-C}$. The most common method is
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33 using ball milling, [14, 15] but the problem is to fabricate uniformly fine particles.
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36 Uniformly fine particles are desirable in $\text{Li}_2\text{S-C}$ cathodes because they promise high
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39 utilization of Li_2S .
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44 So far, there are only a few reports on the preparation of nano-/micro sized $\text{Li}_2\text{S-C}$
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47 without using Li_2S as starting material. One category of methods starts from
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50 nanostructured sulfur-carbon composite or sulfur. Highly reductive chemicals are used
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53 to react with sulfur to prepare nanostructured $\text{Li}_2\text{S-carbon}$ composite. Y. Yang et al. [16]
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56 reported that n-butyllithium ($\text{CH}_3(\text{CH}_2)_3\text{Li}$) reacts with S which is confined in
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mesoporous carbon, to produce Li_2S –mesoporous carbon composite. A similar strategy is spraying lithium-metal powders on S–mesoporous carbon to produce Li_2S , as a chemical lithiation process. [17] C. Nan et al. [8] produced nano-/micro sized Li_2S through reaction of sulfur and lithium triethylborohydride, then prepared a carbon coating on Li_2S via chemical vapor deposition. This method is effective to control the particle size of Li_2S , but expensive and highly reactive chemical is used.

Another kind of method is using the Leblanc process, as reported by L. A. Archer's group. [18] In their method, the first step was the preparation of aerogel in Li_2SO_4 solution. The thus produced aerogel containing dispersed Li_2SO_4 subsequently went through carbon-thermal reduction to produce Li_2S –C. This in situ synthesis represents a low-cost and efficient method, but the capacity stability needs further improvement.

In this work, we applied a new synthesis route to prepare Li_2S –C composite. It has two steps: the first step is to produce Li_2S through the carbon-thermal reduction of Li_2SO_4 (Leblanc process); the second step is to make coating of nitrogen-doped carbon on synthesized Li_2S using an ionic liquid. N-doped carbon is expected to improve the electronic conductivity, which is attractive in case of using insulating Li_2S . [19] This method starting from Li_2SO_4 has the advantage to control the surface area of synthesized Li_2S from two aspects. On one hand, reducing the dimension of Li_2SO_4 can

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3 cause the decrease in particle size of Li_2S . On the other hand, Li_2SO_4 prepared by fast
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6 precipitation is expected to have lots of defects and vacancy; these defects and vacancy
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9 will be remained in synthesized Li_2S to increase its reacting surface area. Through
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12 controlling the dimension and morphology of Li_2SO_4 at micro-scale, this method may
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15 have faster kinetics for Li_2S materials compared with conventional method using
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28 **2. Experimental**

29 **2.1 Materials preparation**

30 **1) Li_2S –C(I) from commercial Li_2SO_4**

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35 1.3 g Li_2SO_4 and 0.58 g ketjen black (KB) were treated by high-energy mechanical
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38 milling (HEMM, Retsch Mixer Mill MM400) for 8 h at the shaking frequency of 25 s^{-1} .
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42 To prevent overheating of the system, a rest time of 30 min was added after each hour of
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45 ball milling. Stainless steel balls of diameter 10 mm were used as milling medium. The
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48 weight ratio between the milling balls and commercial Li_2SO_4 was set to 12:1. Then,
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51 this powder mixture was heat treated at $900\text{ }^\circ\text{C}$ for 2 h under Ar gas at a low flow rate.
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55 The obtained powders were pulverized and milled by HEMM for 1 h. Subsequently,
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0.6 g of the obtained powders were mixed with 0.5 ml ionic liquid, namely 1-ethyl-3-methylimidazolium dicyanamide (EMIM-dca) using a mortar for 20 min inside an Ar-filled glove box. The slurry-like mixture was kept overnight, followed by annealing at 600 °C for 2 h under Ar protection. Finally, the obtained products were pulverized and milled in the glove-box by a mortar for 30 min to obtain the desired $\text{Li}_2\text{S-C(I)}$.

2) $\text{Li}_2\text{S-C(II)}$ from fine Li_2SO_4

0.5 g Li_2SO_4 and 1 ml dimethyl sulfoxide (DMSO) were dissolved in 6 ml deionized water with one drop of HCl. Then, 40 ml of ethanol were quickly added into the aqueous solution. After stirring for 2 min, the mixed solution became an emulsion which was centrifuged at the speed 4000 r min^{-1} for 20 min. The obtained powders were dried under vacuum at 60 °C for 6 h (the vacuum pump was operated only for 0.5 h at the beginning).

The treatment of fine Li_2SO_4 is the same as the process applied to commercial Li_2SO_4 . The only difference is that fine Li_2SO_4 was used.

3) Li₂S–C(III) using Li₂S as starting materials

For comparison, commercial Li₂S was treated by HEMM for 8 h at the shaking frequency of 25 s⁻¹. 0.3 g of ground Li₂S powders were mixed with 0.3 ml EMIM-dca using a mortar for 20 min inside an Ar-filled glove box. Then the slurry-like mixture was kept overnight and treated with annealing at 600 °C for 2 h under Ar protection (the same carbon coating process).

2.2 Electrodes fabrication

Li₂S–C(I) or Li₂S–C(II), acetylene black (AB), and poly(ethylene oxide) (PEO, M_w = 600,000, Aldrich) were mixed according to the weight ratio of 70:20:10 in acetonitrile. PEO was used as binder because the commonly used polyvinylidene fluoride was reported to have low affinity to Li₂S [20]. After being mixed and stirred for 8 h, the well-dispersed viscous slurry was cast onto aluminum foil by using a doctor blade (SNC-280, Yasui Seiki Co. LTD) in a dry room (dew point less than –50 °C). Subsequently, the electrodes were heated to 60 °C for 5 h inside the glove-box, followed by storage under vacuum in the side-room of the glove-box for 1 h. The electrodes had Li₂S mass loading of ~1 mg cm⁻².

2.3 Electrochemical measurements

The electrodes were punched into circular pieces with diameter of 10 mm for cell assembly. Coin cells (2032 type) were prepared using polypropylene separator (Celgard 2500) and lithium metal anode. For the electrolyte, lithium trifluoromethanesulfonate (LiCF_3SO_3 , Aldrich, 99.995%) and tetraethyleneglycol dimethylether (TEGDME, Aldrich, 99%) were mixed in the molar ratio of 1:4 with the addition of 1 wt% LiNO_3 . A charge–discharge system (TOSCAT-3100, Toyo system) was used for constant-current charging and discharging cycling tests. The first cycle was tested at 0.05 C and the following cycles were conducted at individually specified C-rates.

2.4 Materials characterization

The mass loss of the Li_2SO_4 –KB mixture was determined by thermogravimetric analysis (TGA) using a Perkin-Elmer TGA 7 Thermogravimetric Analyzer at the fixed heating rate of $5\text{ }^\circ\text{C min}^{-1}$ in flowing Ar gas. The elemental compositions of the samples were determined by energy-dispersive X-ray spectroscopy (EDX, Miniscope TM3000, Hitachi) in the dry room. Scanning electron microscopy (SEM) images were obtained by field-emission SEM (S-4500S, Hitachi). Both commercial Li_2SO_4 and fine Li_2SO_4

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3 were treated by sputter coating of Pt-Pd to achieve clear images. X-ray diffraction
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6 (XRD, Rint-Ultima III, Rigaku) with Cu K α radiation was used to investigate the crystal
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9 structure of the samples. In order to protect the samples from moisture, the Li₂S–C
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13 powders were put in air-tight sample holder (beryllium specimen holder, Rigaku).
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3. Results and Discussion

Figure 1 is the schematic illustration of the synthesis of Li₂S–C composite using both commercial and fine Li₂SO₄. Through the HEMM treatment, the mixture of Li₂SO₄ and KB is obtained. Subsequently, the most important step to form Li₂S is to execute carbon-thermal reduction. The formation of sulfides via the reduction of sulfates by carbon has been used in the Leblanc process, representing an early industrial process. This reaction, as seen in Eq. 1, is expected to consume carbon and to produce some void space.

The synthesis of Li₂S is not enough, because usually Li₂S needs some coating or embedding into a matrix in order to achieve a high conductivity. Here, the ionic liquid EMIM-dca was selected to make a carbon coating/matrix for synthesized Li₂S. EMIM-dca is expected to produce nitrogen-doped graphitic carbon.[\[21-23\]](#) Note that the lithium ions of Li₂S can strongly interact with electron-donating groups in the carbon precursor. The selected ionic liquid contains a lot of nitrile groups which provide lone-pair electrons to interact with lithium atoms, therefore forming strong adhesion.

TG-DTA analysis under protective Ar atmosphere was done to investigate the

carbon-thermal reaction process. TG shows the change of weight during the heating process, while DTA displays the heat flow at the same time. As shown in Fig. 2a, TG for the mixture of commercial Li_2SO_4 and KB shows the first small stage from 350 °C to 700 °C. Meanwhile, the heat flow fast drops to -40, indicating a strong endothermic process in the first small stage of TG. The endothermic peak of DTA at 580 °C is attributed to the crystal transformation of Li_2SO_4 . The second large stage of TG is observed from 700 °C to 800 °C, accompanied by a flat trough and a followed sharp exothermic peak at 800 °C. As a result, the main reaction is divided into two parts or steps, associated with the first strong endothermic process (sloping range of DTA from 350 °C to 720 °C) and the second exothermic process with a sharp peak at 800 °C. Similar behaviour is observed in other carbon-thermal reductions. For example, in the systems $\text{C} + \text{Fe}_2\text{O}_3$ [24] and $\text{C} + \text{Mn}_3\text{O}_4$ [25], the reductions also involve two reactions: the first endothermic step produces CO; the second exothermic step involves the release of CO_2 . In the present system of commercial $\text{Li}_2\text{SO}_4 + \text{KB}$, whether CO is produced as intermediate product cannot be determined. The detailed reaction path and mechanism is worth being investigated in the future. From 800 °C to 860 °C, the TG curve shows the third small stage, corresponding to a wide exothermic peak with small shoulders in DTA. Because Li_2SO_4 has a melting point of 845 °C, the wide exothermic peak at

850 °C can be attributed to the reductive reaction of bulk Li_2SO_4 . Bulk Li_2SO_4 cannot react with carbon until it melts and thereby increases its contact surface with carbon. According to the TG-DTA results, we choose the reaction temperature of 900 °C with corresponding weight loss of 68%. Figure 2b shows the TG-DTA curves of fine Li_2SO_4 and KB. At the beginning, it displays a weight loss of 8.6% and sharp endothermic peak at 106 °C. This change is due to the loss of crystal water from fine Li_2SO_4 . In the following temperature, the TG-DTA curve of fine Li_2SO_4 shows similar trend to that of commercial Li_2SO_4 .

Figure 3 illustrates the morphological evolution of the samples during the preparation process. The commercial Li_2SO_4 has random particle-size distribution, as seen in Fig. 3(a). Large particles of Li_2SO_4 with diameters of up to 30 μm were frequently observed. Because of its non-polar nature, carbon does not interact favorably with polar Li_2SO_4 . HEMM is used to punch Li_2SO_4 and KB together. Figure 3(b) shows aggregated bulk particles. The mixture of Li_2SO_4 and KB looks uniform and dense with the help of HEMM. In addition, there is an isolated particle. It looks white in the SEM image and is outlined by the dashed yellow circle in Fig. 3(b). The abrupt brightness change of this particle can be attributed to its poor conductivity. This particle has low carbon content

as confirmed by EDX (not shown here), and is likely isolated Li_2SO_4 . After annealing at 900 °C, the morphology changes significantly as a result of carbon (KB) consumption and the formation of Li_2S during the carbon-thermal reduction, as seen in Fig. 3(c). Aggregation is observed over the entire area of the image. Some big crystal-like particles with smooth surface consist of synthesized Li_2S with diameter of 6–10 μm . Other particles with rough surface are mixtures or composites of unreacted KB and synthesized Li_2S . Figure 3(d) shows the morphology of Li_2S –C(I) after carbon coating at 600 °C. The diameter of a typical particle is ~10 μm . Some fold is observed at the particle surface, which is very likely carbon produced from the ionic liquid.

The composition of Li_2S –C(I) synthesized from commercial Li_2SO_4 was determined by EDX analysis (Table 1). Li_2S –C(I) contains four elements: C, S, O, and N. Because the element Li cannot be detected using EDX, the Li amount is calculated based on the stoichiometry of Li_2S . From the weight fractions of the various elements, the Li_2S content in the composite Li_2S –C(I) is ~53.3 wt%.

Figure 4(a) represents the charge–discharge curves of Li_2S –C(I) prepared from commercial Li_2SO_4 . During the initial charge process, a plateau starts from the high voltage of 3.5 V and soon slopes down to 3.3 V, forming a small hump. The voltage

hump is thought of being originated from phase nucleation of polysulfides. [26, 27]

Because Li_2S suffers from high charge-transfer resistance and intrinsic electronic insulation, usually a high over potential is needed for the initial charge process of Li_2S .

In the following charge process, the voltage sags and swells, resulting in waves in the overall charge plateau. This phenomenon is probably related to impurities in the cathode.

As indicated later in the XRD patterns, unreacted Li_2SO_4 persists as impurity. Because inactive Li_2SO_4 acts as isolated point or area for electron and Li^+ ion transport, it likely causes the sudden falling of the charging voltage. After adding the suitable redox mediator in the electrolyte to weaken the effect of Li_2SO_4 , this unusual shape of initial charge curve turns into normal one, as shown in Fig. S1 (supporting information).

During the 1st discharge, a large irreversible capacity is observed. This phenomenon is attributed to the dissolution of polysulfides, which is the main reason for the capacity fading of Li-S batteries. In the second cycle, the voltage hump still exists at the beginning of the charge plateau, but the charge plateau is at 2.3 V, much lower than at 3.4 V observed in the first cycle. According to the literature [26, 28], the polarization of Li_2S decreases once the generation of soluble polysulfide ions has been initiated.

Figure 4(b) presents the cycle performance of $\text{Li}_2\text{S}/\text{C}(\text{I})$ (without carbon coating) and $\text{Li}_2\text{S}-\text{C}(\text{I})$ (with carbon coating) prepared from commercial Li_2SO_4 . A large capacity

drop is observed in both samples between the 1st and 2nd cycle because of the different C rates: the 1st cycle has been performed at 0.05 C and the following cycles are at 0.1 C. Both samples show slow capacity fading upon cycling at 0.1 C and low coulombic efficiency (CE) at the initial one or two cycles. The Li₂S-C(I) with carbon coating shows higher discharge capacity than Li₂S/C(I) without carbon coating. The increase of capacity is attributed to the improved electronic conductivity by carbon coating. As shown in Fig. 4(c), the Nyquist plot is composed of one depressed semicircle in the high frequency region and one straight line in the low frequency region. The diameter of the semicircle corresponds to the charge transfer resistance at the interface. The Li₂S-C(I) with carbon coating has a smaller semicircle compared to Li₂S/C(I) without carbon coating. This indicates that carbon coating helps to reduce the charge transfer resistance and enhance the kinetics.

Figure 5 illustrates the morphological evolution of fine Li₂SO₄ during the synthesis process, as observed by SEM. Figure 5(a) shows the typical particles of commercial Li₂SO₄, with random particle-size distribution. Bulk particle with diameter of 15 μm is observed. After the multi-solvent recrystallization process, the obtained particles have much smaller particle size, as shown in Fig. 5(b), in strong contrast to commercial Li₂SO₄. From the high-magnification image shown in Fig. 5(c), the

prepared fine particles have the average particle size of 2 μm . After the first annealing at 900 $^{\circ}\text{C}$, the obtained $\text{Li}_2\text{S}/\text{C}(\text{II})$ powders in Fig. 5(d) have an average particle size of 3 μm , smaller than 10 μm observed in case of $\text{Li}_2\text{S}/\text{C}(\text{I})$ prepared from commercial Li_2SO_4 . Meanwhile, the $\text{Li}_2\text{S}/\text{C}(\text{II})$ powders obtained from fine Li_2SO_4 also display less aggregation. Using fine particles of Li_2SO_4 reduces the particle size of Li_2S . This means that our idea works well. Figure 5(e) displays the morphology of $\text{Li}_2\text{S}-\text{C}(\text{II})$ after carbon coating. $\text{Li}_2\text{S}-\text{C}(\text{II})$ has a melt-like surface, which is carbon coating originating from the ionic liquid EMIM-dca. However, the powders of the final product $\text{Li}_2\text{S}-\text{C}(\text{II})$ show some aggregation. This aggregation can only result from the ionic-liquid coating. Possibly, the ionic liquid acts as glue and sticks the $\text{Li}_2\text{S}/\text{C}(\text{II})$ powders. During the second coating process, the ionic liquid undergoes condensation and carbonization, thus forming an interconnecting carbon network between the powders.

Figure 5(f) shows the EDX spectrum of $\text{Li}_2\text{S}-\text{C}(\text{II})$. It also contains four elements: C, N, O, and S. The red line indicates the position of element aluminium since an aluminium stage was used. According to the weight fractions of the various elements, the Li_2S content in the composite $\text{Li}_2\text{S}-\text{C}(\text{II})$ is calculated to be 55.5 wt% (as shown in Table 1). Because large fraction of oxygen is remained in the $\text{Li}_2\text{S}-\text{C}(\text{II})$, X-ray Photoelectron

Spectroscopy was used to determine the oxide phases. As seen from the Fig. S2 (supporting information), $-\text{SO}_4$ and $-\text{CO}_3$ chemical bonding exist on the surface of $\text{Li}_2\text{S}-\text{C}(\text{II})$. $-\text{SO}_4$ comes from the unreduced Li_2SO_4 , as verified later by XRD. For $-\text{CO}_3$, possibly due to incomplete carbon-thermal reaction, some carbon is oxidized to form $-\text{CO}_3$ instead of CO_2 (in Eq. 1).

Figure 6(a) shows the XRD pattern of the fine-grain Li_2SO_4 sample obtained through the process of multi-solvent recrystallization. The peaks of these fine particles accord well with the diffraction of $\text{Li}_2\text{SO}_4 (\text{H}_2\text{O})$ (JSPDS card No. 84-0647), except for the strongest peak at 22 degree, as indicated by the dashed line with arrows. The sharpest peak can be assigned to the crystal structure of Li_2SO_4 (JSPDS card No. 75-0929). This means that the fine particles prepared by multi-solvent recrystallization have two different crystal structures, namely $\text{Li}_2\text{SO}_4 (\text{H}_2\text{O})$ and Li_2SO_4 . Figure 6(b) displays the structural evolution during the two steps. Li_2S powders (JSPDS card No. 23-0369) were formed during the 1st annealing process at 900 °C. This is in agreement with the TG-DTA results indicating that carbon-thermal reduction happens at temperatures below 900 °C. After the 2nd carbon-coating process, the diffraction peaks of Li_2S are much sharper, indicating that the crystallinity increased. Both samples shown in Fig. 6(b)

exhibit small peaks at 22° , the angular position at which Li_2SO_4 has its sharpest peak.

Therefore, in the product of $\text{Li}_2\text{S-C(II)}$, some Li_2SO_4 exists as impurity. This Li_2SO_4 possibly lost contact with KB carbon and then cannot be reduced. The confirmation of impurity Li_2SO_4 also accounts for the high oxygen content in $\text{Li}_2\text{S-C(II)}$.

Figure 7(a) shows the charge–discharge curves of $\text{Li}_2\text{S-C(II)}$ prepared from fine Li_2SO_4 .

During the initial charge process, a small voltage hump is also observed at the beginning. However, the voltage is only 2.85 V, much smaller than 3.5 V observed in $\text{Li}_2\text{S-C(I)}$ prepared from commercial Li_2SO_4 . As mentioned above, a high over potential is usually needed for the initial charge process of Li_2S . The lower over potential for the initial charging of $\text{Li}_2\text{S-C(II)}$ indicates that reducing the particle size helps to improve the charge-transfer resistance, likely through shortening the diffusion distance for lithium ions. Following this voltage hump, the charge voltage gradually increases to 3.8 V, and a new oxidation plateau appears. This new plateau is related to undesired shuttling reactions, which occur only after complete oxidization of Li_2S to sulfur. [27]

During the 2nd charge–discharge, $\text{Li}_2\text{S-C(II)}$ exhibits a similar behavior like $\text{Li}_2\text{S-C(I)}$.

Figure 7(b) compares the cycle performance of $\text{Li}_2\text{S-C(II)}$ and $\text{Li}_2\text{S-C(I)}$ at 0.2 C.

The solid symbols represent the capacity, while the corresponding hollow symbols show

the CE. The two samples show slow capacity fading at 0.2 C upon 50 cycles, except for the 1st cycle owing to the different current density. This capacity loss during long cycles is due to dissolution of polysulfides and cumulative deposition of insulating Li₂S₂/Li₂S on electrode surface (Figure S3 in supporting information). Li₂S–C(II) outperforms Li₂S–C(I) in discharge capacity. One possible reason is that fine Li₂SO₄ enables smaller particle size for Li₂S/C and achieves more uniform distribution of Li₂S in the carbon matrix. The improved distribution of Li₂S is better suited to enhance the utilization of Li₂S. Concerning CE, both samples show low efficiency in the first two formation cycles, and then maintain a high CE above 95%. Compared to the work of L. A. Archer's group [18], the Li₂S–C composite in our work shows more stable cycle stability and much higher coulombic efficiency, especially in view of the fact that our cycling was done at lower C rate. However, their capacity is somewhat higher than the capacity observed in this work.

There are two possible reasons for the relatively low capacity in our Li₂S–C composite. The first reason is the capacity loss due to the dissolution of polysulfides, especially in the first cycle. A large irreversible capacity of 300 mAh g⁻¹ was observed in the 1st cycle. The second reason is the Li₂SO₄ impurity. The capacity is calculated based on the mass of elemental Li and S. However, some Li and S element exist in the

form of Li_2SO_4 , and cannot contribute to the capacity. So the impurity Li_2SO_4 lowers down the usage of Li_2S and capacity. These two reasons also point out the ways to further improve the capacity of our $\text{Li}_2\text{S-C}$ composite. One way is reducing the particle size of Li_2S to the range of 500 nm-1 μm . With distribution of particle size in this range, $\text{Li}_2\text{S-C}$ composite is expected to have desired structure to hinder the dissolution of polysulfides. Another way is optimizing the experimental conditions such as milling and heat treatment to reduce the amount of unreacted Li_2SO_4 .

As ground Li_2S by ball milling is commonly used as starting materials, the $\text{Li}_2\text{S-C(II)}$ is also compared to $\text{Li}_2\text{S-C(III)}$ prepared from ground Li_2S . From the impedance spectra in the Fig. 7(c), the charge transfer resistance of $\text{Li}_2\text{S-C(II)}$ is smaller than $\text{Li}_2\text{S-C(III)}$ (90 Ω mg compared to 120 Ω mg). This means that the kinetics was improved by this method. According to the calculations from the impedance data (Table S1 in supporting information), the time constant of the interfacial impedance for both samples is similar. It indicates that the reaction itself does not change in these two different methods. Since the time constant is similar, the smaller charge transfer resistance can be attributed to larger reacting surface area. Fine Li_2SO_4 prepared by fast precipitation is expected to have lots of defects and vacancy. During the structural transformation from Li_2SO_4 to Li_2S , defects and vacancy will remain. This increases the

reacting surface area for synthesized Li_2S as compared with the Li_2S particles prepared by milling. The rate performances of these two samples are also compared, as shown in Fig. 7(d). Both samples show similar capacity at 0.1C, but $\text{Li}_2\text{S-C(II)}$ from fine Li_2SO_4 shows higher capacity than $\text{Li}_2\text{S-C(III)}$ at 0.2 C, 0.5 C and 1 C. Meanwhile, the charge-discharge profiles (Figure S4 in supporting information) show that the $\text{Li}_2\text{S-C(III)}$ from ground Li_2S has higher over potential with the increased C rate. So the $\text{Li}_2\text{S-C}$ composite synthesized from fine Li_2SO_4 performs better in the fast charge-discharge process. As a result, using fine Li_2SO_4 as starting materials has the advantage of increasing the kinetics for Li_2S .

4. Conclusion

A new synthesis approach was developed to prepare $\text{Li}_2\text{S-C}$ composite using Li_2SO_4 as starting material. Li_2S was firstly prepared via carbon-thermal reduction of Li_2SO_4 , and further coated or composited with N-doped carbon from ionic liquid. In order to improve the morphologies and distributions in particle sizes, a multi-solvent recrystallization was used to reduce the particle size of starting materials Li_2SO_4 . The obtained fine Li_2SO_4 with average diameter of 2 μm enables particle-size control during the carbon-thermal reduction process. As a result, $\text{Li}_2\text{S/C(II)}$, the product of the first

annealing step, has the average particle diameter of $\sim 3\ \mu\text{m}$, much smaller than that observed in samples prepared from commercial Li_2SO_4 . Using fine Li_2SO_4 also significantly reduces the charge voltage in the initial charge process. Moreover, this reduction of the particle size of the starting material improves the capacity. Finally, $\text{Li}_2\text{S-C(II)}$ prepared from fine Li_2SO_4 displayed the stable capacity of $350\ \text{mAh g}^{-1}$ at $0.2\ \text{C}$ over 50 cycles. This method using fine Li_2SO_4 becomes more interesting as it shows faster kinetics than that using ground Li_2S as starting materials. Further improvement of this capacity is expected by reducing the particle size of fine Li_2SO_4 and removing the impurity phase which consists of unreacted Li_2SO_4 .

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Figure Captions

Figure 1. Schematic of the synthesis of $\text{Li}_2\text{S-C}$ composite. Both commercial and fine Li_2SO_4 were used as starting materials.

Figure 2. TG-DTA curves for: (a) commercial Li_2SO_4 and KB, (b) fine Li_2SO_4 and KB.

Figure 3. SEM images showing the morphology of: (a) commercial Li_2SO_4 , (b) mixture of commercial Li_2SO_4 and KB after high energy mechanical milling, (c) as-synthesized $\text{Li}_2\text{S/C(I)}$ after the 1st annealing at 900 °C; (d) $\text{Li}_2\text{S-C(I)}$ after the 2nd coating process at 600 °C.

Table 1. EDX composition of $\text{Li}_2\text{S-C}$ prepared from different starting materials ($\text{C} + \text{S} + \text{O} + \text{N} = 100\%$, the Li amount is calculated from the percentage of S based on the stoichiometry Li_2S . The Li_2S amount is calculated according to $(\text{Li} + \text{S})/(\text{Li} + \text{S} + \text{C} + \text{O} + \text{N})$).

Figure 4. (a) Charge–discharge curves of $\text{Li}_2\text{S-C(I)}$ prepared from commercial Li_2SO_4 ; (b) comparison of the 0.1C cycle performance for $\text{Li}_2\text{S-C(I)}$ and $\text{Li}_2\text{S/C(I)}$ ($0.1 \text{ C} = 116.6 \text{ mA g}^{-1}$, the 1st cycle is performed at 0.05C); (c) Impedance spectra before cycling for $\text{Li}_2\text{S-C(I)}$ and $\text{Li}_2\text{S/C(I)}$.

Figure 5. SEM images presenting the sample morphologies: (a) commercial Li_2SO_4 ,

(b) low-magnification image of fine Li_2SO_4 , (c) high-magnification image of fine Li_2SO_4 , (d) as-synthesized $\text{Li}_2\text{S}/\text{C}(\text{II})$ after the 1st annealing at 900 °C, (e) $\text{Li}_2\text{S}-\text{C}(\text{II})$ after the 2nd coating process at 600 °C, (f) corresponding EDX spectrum of $\text{Li}_2\text{S}-\text{C}(\text{II})$.

Figure 6. XRD characterization of: (a) the mixture of fine Li_2SO_4 and KB, (b) the structure evolution during the two annealing processes.

Figure 7. $\text{Li}_2\text{S}-\text{C}(\text{II})$ prepared from fine Li_2SO_4 : (a) charge–discharge curves, (b) cycle performance at 0.2 C (0.2 C = 233.2 mA g⁻¹, the 1st cycle is at 0.05 C). (c) Impedance spectra for $\text{Li}_2\text{S}-\text{C}(\text{III})$ prepared from ground Li_2S and $\text{Li}_2\text{S}-\text{C}(\text{II})$. The unit is ohm × mg because the value is regulated by the mass of Li_2S . (d) Specific capacity of $\text{Li}_2\text{S}-\text{C}$ cathodes cycled at various C rates from 0.1 C to 1 C.

New modification: **peak at 23° disappears**

Figure I. XRD characterization of: (a) new modification of the heating process- not detection of Li_2SO_4 ; (b) the old process.

Figure 1

Figure(s)

Figure(s)

Figure 3

Figure(s)

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Figure(s)

Figure 5a

Figure(s)

Figure 5c

Figure 5d

Figure 5e

Figure(s)

Figure 6a

Figure 6b

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Table 1

	C	S	O	N	Calculated Li ₂ S
	wt%	wt%	wt%	wt%	wt%
Li ₂ S-C(I) from commercial Li ₂ SO ₄	21.6	43.6	27.4	5.8	53.3
Li ₂ S-C(II) from fine Li ₂ SO ₄	20.2	46.3	29.3	3.6	55.5